Patented July 11, 1939 2,165,607

UNITED STATES PATENT OFFICE

2,165,607

METHOD OF RECOVERING THE VALUES FROM ORES

George Blow, New York, N. Y.

No Drawing. Application March 13, 1936, Serial No. 68,781

13 Claims. (Cl. 209—172)

This invention relates to improvements in the method of separating the valuable constituents of an ore from those which are less valuable or worthless and has for its object the recovery of maximum values in the ore at minimum cost.

Another object of this invention is to provide a novel procedure for recovering the values in an ore by utilizing the difference in specific gravity between the various minerals composing the ore.

Another object of this invention is to provide a new and economical method for overcoming the unfavorable influence of water on the gravity separation of mineral particles in a liquid which is not miscible with water, and for recovering the heavy separating liquid so that it may be used over again.

Another object of this invention is to insure the complete wetting of some of the constituents of an ore by the liquid in which the gravitational separation is to take place by the utilization of certain principles of surface tension.

Another object of this invention is to provide a novel process for the utilization of certain principles of surface tension in the treatment of the divided constituents of an ore after separation by gravity to free these constituents of the liquid in which the gravitational separation took place.

Other and further objects of this invention will appear herafter as the invention is described.

All ores, whether metallic or non-metallic, are aggregates of minerals in which the valuable portion to be recovered, whether lead, gold, barite, or fluorite, is generally in much smaller quantity than the worthless gangue, such as quartz or limestone. The separation of the valuable from the worthless portion is the art of ore dressing and employs such familiar processes as jigging, tabling, cyanidation, and flotation. As a preliminary step, all methods of ore dressing require crushing and grinding of the ore to liberate the valuable mineral from the waste minerals; that is, the ore is ground until the valuable minerals are broken free from any attached or enclosing gangue. The subsequent treatment is then determined by the class of ore to be treated. For ores of the base metals and non-metallics the valuable portion is recovered as a "concentrate" and the worthless is discarded as "tailings". Thus for a simple lead ore composed of galenite and quartz there is produced a lead concentrate, consisting of the lead mineral from which the lead is later recovered, and tailings consisting of finely-divided quartz.

In gravitational separation of values from ores the difference in specific gravity between the various minerals composing the ores is utilized. The metallic minerals, and particularly the sulphides, are heavier than their associated gangue minerals. This is shown by the following example:

Valuable minerals	Specific gravity	Gangue minerals	Specific gravity
Galenite, PbS	7.4	Quartz	2.6
Pyrite, FeS_2	4.9	Hornblende	2.9
Chalcocite, Cu_2S	5.5	Feldspar	2.7
Gold, Au	19.3	Mica	2.8

It is a well known law of physics that bodies lighter than a liquid will float therein, while those heavier than a liquid will sink. Therefore, if an ore is sufficiently ground to free the valuable minerals and is immersed in a liquid heavier than the gangue and lighter than the valuable minerals, the gangue will float on the surface, while the heavier minerals will sink to the bottom. As an example, if the liquid has a specific gravity of 3.26 and the ground ore consists of free pyrite (sp. gr. 4.9) and quartz (sp. gr. 2.6), the pyrite will sink and may be collected from the bottom of the vessel, while the quartz will float and may be drawn off at the top. The action is positive and a perfect separation is accomplished, and either portion may be recovered for its values. It follows that any liquid with a specific gravity intermediate between the specific gravities of two minerals will separate such minerals, irrespective of their size, by floating the lighter and submerging the heavier when they are immersed in the liquid. Several liquids of high specific gravity are available for this purpose and among these may be mentioned the following:

1. Methylene iodide, CH_2I_2, sp. gr. 3.26 to 3.32 at 15° C.

2. Sonstadt's solution, a saturated solution in water of potassium iodide and mercuric iodide, sp. gr. 3.08 at 12° C.

3. Klein's solution, borotungstate of cadmium, $9WO_3B_2O_3 2CdO.2H_2O$—16 Aq., sp. gr. 3.28 at 15° C.

4. Acetylene tetrabromide, $C_2H_2Br_4$ sp. gr. 2.96 at 20° C.

Each of these liquids has its own chemical and physical properties. In order to describe the present invention more clearly, the use of methylene iodide will be taken as an example. It is distinctly understood, however, that the application of this invention to the treatment of ores is

not limited to any specific liquid and that any liquid possessing the required specific gravity and other suitable properties may be used.

Methylene iodide is a clear yellow liquid and at room temperatures is as fluid and mobile as water in spite of its high specific gravity. The specific gravity is 3.26 to 3.32 and it will therefore float all of the common gangue minerals. It is not miscible nor can it be diluted with water. It is soluble in any proportion in either benzol or toluol. These solvents are much lighter than methylene iodide and, consequently, when they or either of them is or are mixed with it the specific gravity is decreased. This is a valuable property, for it affords a means of changing the specific gravity of the liquid to separate minerals which in themselves have only a slight difference in specific gravity. Thus, if it is desired to separate two minerals having specific gravities of 2.6 and 3.0 respectively, the proper proportion of benzol can be added to methylene iodide to give the latter a specific gravity of 2.8, which lies between the values for the two minerals.

It is evident that when a heavy liquid is used to separate the constituents of an ore the liquid wets each particle of both concentrate and tailing, particularly if the ore is ground in the dry state, and this liquid must be removed from both products, otherwise there is a constant loss of the separating medium which would make the cost of the process prohibitive. However, most ores are ground wet rather than dry, and this brings in another condition when separation of the various constituents is to be effected by means of a heavy liquid. In the usual practice of wet grinding, all of the mineral particles become thoroughly wet with water. The material to be separated is therefore a wet pulp consisting of various size mineral particles in a vehicle of water. When such a pulp is immersed in a heavy immiscible liquid which is intermediate in specific gravity between the constituents of the ore it is desired to separate, the large heavier particles sink and the large lighter particles float. The smaller particles, however, being thoroughly wet, are drawn together by the surface tension of the water. Thus a particle of valuable mineral and a particle of waste may become encased in a common water film so that they cannot separate under the action of gravity. Furthermore, the presence of a film of water on a mineral particle, being lighter than both the mineral and the separating liquid, may be sufficient to reduce the relative weight of the particle so that it will float rather than sink. It is therefore clear that in order to separate minerals of different specific gravity which have been wet by water in the grinding process such water must be displaced in order to permit a separation when the wet mixed pulp is immersed in a heavy liquid immiscible with water. The water bondage must be broken so that the various particles are free to separate.

From the foregoing it will be seen that there are two steps necessary for the successful gravity separation of mineral particles in heavy liquids:

1. When the ore is so ground in water that the mineral particles become wet thereby, two or more particles may be encased in a common film of water. This encasement must be broken so that they may separate by gravity. In this step the water bondage is broken by displacing the water from one class or more of the mineral constituents of the ore. In other words, some or all of the particles become wet by the separating liquid instead of water. When the ore is dry ground there is, of course, no water encasement and all particles become wet by the separating liquid and readily separate.

2. The second step consists of removing the separating liquid from the surface of any of the mineral particles which have become wet thereby. This is necessary in order to recover the separating liquid so that it may be returned to the bath for further use.

In each of the above steps the action is the displacement of one liquid on a solid surface by another liquid with which it is immiscible. The physical principle underlying this action is as follows: One liquid may be made to displace on a solid surface another liquid with which it is immiscible by decreasing the liquid-liquid angle of contact with the solid on the side of the displacing liquid. When two immiscible liquids are in contact with a solid, the plane of the interface between the two liquids makes an angle with the surface of the solid. This is the liquid-liquid angle of contact. Decreasing this angle on the side of the displacing liquid causes the displacement of one liquid by another on the solid surface. There are three methods by which this can be accomplished, which will be described in turn.

The first method consists of changing the surface condition of one class of solids in the ore mixture or pulp. It is well known in the ore flotation process which is now widely applied in practice that the angle of contact of water on the surface of a sulphide mineral can be increased by the addition of suitable agents to the water. This is due to a change in the surface condition of the solid through adsorption of certain constituents of the chemical agent employed. Some of the agents which have this effect are a long series of xanthates. For instance, if a small quantity of potassium ethyl xanthate is added to water, the angle of contact on sulphide surfaces is measurably increased. In the present case we are concerned with two liquids instead of one, but it is evident that if the angle of contact of one liquid is increased the other angle of contact must be decreased. In other words, if the angle for water is increased the angle for methylene iodide is decreased. This is decreasing the liquid-liquid angle of contact on the side of the displacing liquid. If, therefore, a small quantity of potassium ethyl xanthate is added to the water which wets the mineral particles, such water will be displaced by the heavy separating liquid on the surface of the sulphide particles. The water encasement is thereby broken and the particles are free to separate in the bath of heavy liquid.

The second method for the displacement of water on mineral particles consists of increasing the surface tension of the water of the pulp. This produces an increase in the angle of contact of water on a solid surface, for it decreases the work of adhesion of the water for the solid. When two liquids are involved as in the present instance, increasing the angle of contact of the water decreases the liquid-liquid angle of contact on the side of the displacing liquid, as already explained. There are a number of chemical compounds which have the property of increasing the surface tension of water, including most of the inorganic salts. Therefore, if a small quantity of calcium chloride or copper sulphate is added to the water, the surface tension of the water is increased and the liquid-liquid angle of contact is decreased on the side of the methylene iodide and the water is displaced so that any mineral particles encased by a film of water are

freed so that they may separate in the heavy liquid bath.

The third method to cause the displacement of water on mineral particles by the separating liquid consists of decreasing the surface tension of the separating liquid itself. A decrease in the surface tension of the separating liquid produces an increase in the work of adhesion of the liquid for the solid and therefore a decrease in the angle of contact relative to water. This is a decrease of the liquid-liquid angle of contact on the side of the separating liquid so that the water is displaced and any bondage between the mineral particles is broken. Decreasing the surface tension of the separating liquid is accomplished by the addition of volatile solvents. For instance, the addition of small quantities of benzol or toluol to methylene iodide or other heavy halogen hydrocarbons decreases the surface tension of such liquids. At the same time there is, of course, a decrease in the specific gravity of the liquid, but there is generally sufficient latitude in this respect still to have the liquid a satisfactory separating medium. It is also known that an electric current decreases the surface tension of mercury and there are possibilities of applying this principle to other heavy liquids when used for the separation of minerals.

It should be noted from the foregoing that any one or a combination of the methods described may be used to cause displacement of water on mineral particles by the separating liquid so that they may be freed to act under the force of gravity in the separating bath.

The second step of the process of the present invention consists of displacing the separating liquid from the surface of any of the mineral particles which may have become wet thereby due to submergence in the separating bath. It has been pointed out that in the first step some or all of the mineral particles must become wet by the heavy liquid in order to permit their separation. All of this liquid which adheres or clings to the mineral products of the separation must therefore be displaced and recovered. This displacement is accomplished by utilizing the same principle described in the third method above, that is, decreasing the surface tension of the displacing liquid. The heavy liquid is displaced by treating the products of the separating bath with water to which has been added a suitable agent to produce a decrease of its surface tension. There are a number of organic compounds, notably soaps and synthetic alcohols, which have the property of materially reducing the surface tension of water. Therefore, if a small quantity of a suitable soap is added to water and this solution is used to treat the products of separation, the heavy liquid is displaced from the surface of the mineral particles and, being heavier than and immiscible with the water, it may be readily collected and returned to the separating bath. The recovery of the heavy separating liquid which adheres to the mineral particles or may become entrained with the products of the process is accomplished by treating such products with water that has had its surface tension decreased. Here, again, the action is one of displacement, for the separating liquid is not washed off or taken into solution but is physically removed under the action of the forces described.

It is to be understood that as used herein, the words "heavy liquid", or "heavy separating liquid" mean and are intended to mean a liquid whose specific gravity is greater than water and is intermediate the specific gravities of the particles of ore to be separated, that is, greater than the specific gravity of some of the particles and less than the specific gravity of some of the other particles, whereby lighter particles will float and heavier particles will sink therein.

In describing this process, the heavy minerals have been designated as sulphides, as this is the most common type found in ores. It is to be distinctly understood that the process is not confined to the recovery of such minerals alone but is applicable to the treatment of any ore in which the constituents to be separated have a sufficient difference in specific gravity. Thus it may be employed for gold, copper, or silver ores, where the metal is found in the native state, or it may be used for the separation of non-metallic minerals. Under certain circumstances the valuable portion which it is desired to recover may be that portion which floats rather than the portion which sinks. In other cases both products may have value. It is the separation of the components of a mechanical mixture based on difference in specific gravity which is significant and not restriction of the process to any given class of material.

The apparatus required consists of one or more baths of the heavy liquid with means for immersing the pulp, adding any agents desired, removing the floated and sunken products, and washing these free of the separating medium. Such apparatus may be of any suitable design and is not a part of this invention. It may be noted, however, that the separation may be effected in one step or in several stages. If immersion in a single bath does not give a sufficiently clean separation, the operation may be repeated until the desired result is attained.

Having described my invention, what I claim is:

1. In a gravity process of separating ore particles in a separating liquid whose specific gravity is intermediate the gravities of the particles to be separated, the steps of coating the ore particles with a film of wetting liquid, then immersing the wetted ore particles in a gravity separating liquid immiscible with the wetting liquid, the liquid-liquid angle of contact of the two liquids with the ore particles being such that the separating liquid disrupts and displaces the wetting film on the ore particles, whereby said particles become wetted with the separating liquid and sink or float therein according to their respective specific gravities, and then removing the film of separating liquid from the ore particles by subjecting them to the action of a displacing liquid immiscible with the separating liquid, the liquid-liquid angle of contact of the two liquids being such that the displacing liquid will disrupt and displace the film of separating liquid on the ore particles.

2. In a gravity process of separating ore particles, the steps of immersing and wetting the ore particles in a separating liquid having a specific gravity intermediate the specific gravities of the particles to be separated, whereby the particles are wetted with the separating liquid and sink or float therein, and then subjecting separated particles to the action of a liquid immiscible with the separating liquid and having a liquid-liquid angle of contact that will disrupt the film of separating liquid on the ore particles and remove the separating liquid therefrom.

3. In a gravity process of separating ore particles, the steps of wetting the ore particles with water, immersing the wetted particles in a sepa-

rating liquid having a specific gravity intermediate the specific gravities of the ore particles to be separated and acting to displace the water on the ore particles and replace the same with the separating liquid, whereby some of the ore particles sink and some of them float in the separating liquid, and then subjecting the separated particles wet with the separating liquid to the action of a liquid immiscible with the separating liquid and acting to displace the separating liquid on the ore particles.

4. In a process of separating ore particles of differing specific gravities in a separating liquid whose specific gravity is intermediate the specific gravities of the particles to be separated, the steps of wetting the ore particles with a liquid, and then immersing the wetted particles in a separating liquid immiscible with the wetting liquid and having a liquid-liquid angle of contact that will disrupt the wetting film on the particles, whereby the particles are wetted with the separating liquid.

5. In a gravity process of separating ore particles in a separating liquid whose specific gravity is intermediate the gravities of the particles to be separated, the steps of coating the ore particles with a film of wetting liquid, and then displacing the wetting film by immersing the wetted ore particles in a gravity separating liquid immiscible with and having a surface tension less than that of the wetting liquid, and having a liquid-liquid angle of contact that disrupts the wetting film, whereby the wetting liquid on the particles is displaced by the gravity separating liquid and the particles are left free to sink or float therein according to their respective specific gravities.

6. In a process of separating ore particles of differing specific gravities in a separating liquid whose specific gravity is intermediate the specific gravities of the particles to be separated, the steps of wetting the ore particles with a liquid containing a xanthate, and then immersing the wetted particles in a separating liquid immiscible with the wetting liquid and having a liquid-liquid angle of contact that will disrupt the wetting film on the particles, whereby the particles are wetted with the separating liquid.

7. In a gravity process of separating finely comminuted ore particles in a separating liquid whose specific gravity is intermediate the gravities of the particles to be separated, the steps of coating the ore particles with a film of wetting liquid containing a xanthate, and immersing the wetted ore particles in a gravity separating liquid immiscible with and having a surface tension sufficiently less than that of the wetting xanthate liquid to disrupt the wetting film, whereby the wetting liquid on the particles is displaced by the gravity separating liquid and the particles are left free to sink or float therein according to their respective specific gravities.

8. In a gravity process of separating ore particles in a separating liquid whose specific gravity is intermediate the gravities of the particles to be separated, the steps of coating the ore particles with a film of wetting liquid, and then immersing the wetted ore particles in a gravity separating liquid immiscible with the wetting liquid, the liquid-liquid angle of contact of the two liquids with the ore particles being such that the separating liquid disrupts and displaces the wetting film on the ore particles, whereby said particles become wetted with the separating liquid and sink or float therein according to their respective specific gravities.

9. In a gravity process of separating ore particles in a separating liquid whose specific gravity is intermediate the gravities of the particles to be separated, the steps of coating the ore particles with a film of wetting liquid, and then immersing the wetted ore particles in a gravity separating liquid immiscible with the wetting liquid and that will displace the wetting liquid from the particles, whereby said particles become wetted with the separating liquid and are free to sink or float therein according to their respective specific gravities.

10. In a gravity process of separating ore particles in a separating liquid whose specific gravity is intermediate the gravities of the particles to be separated, the steps of coating the ore particles with a film of wetting liquid, selecting a gravity separating liquid having a specific gravity intermediate the specific gravities of the ore particles to be separated, adding a surface-tension-decreasing agent thereto, and then immersing the wetted ore particles in said separating liquid, whereby the separating liquid displaces the wetting film on said particles and the particles are free to sink or float therein according to their respective specific gravities.

11. In a gravity method of separating ore particles, the steps of wetting the particles with a wetting liquid and then immersing the wetted particles in a separating liquid immiscible with the wetting liquid and whose specific gravity is intermediate the specific gravities of the particles to be separated, one of said liquids containing an agent decreasing the normal liquid-liquid angle of contact of the liquids on the side of the separating liquid to the disrupting point of the wetting liquid.

12. In a process of gravity separation of ore particles, the steps of preparing a wetting liquid and a gravity separating liquid immiscible with the wetting liquid and whose specific gravity is intermediate the specific gravities of the particles to be separated, decreasing the normal liquid-liquid angle of contact of said liquids on the side of the separating liquid to the disrupting point of the wetting liquid, wetting the ore particles with the wetting liquid, and then immersing the wetted particles in the separating liquid.

13. In a process of separating ore particles of differing specific gravities in a separating liquid whose specific gravity is intermediate the specific gravities of the particles to be separated, the steps of wetting the ore particles with a liquid, and then immersing the wetted particles in a separating liquid whose angle of contact with the wetted particles is so small that the separating liquid displaces the wetting liquid, whereby the ore particles are wetted with the separating liquid.

GEO. BLOW.